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Title: Implemented advance Surface-Hopping functional in time dependent Density Functional Theory (TDDFT) simulator package for modeling of nonlinear X-ray spectroscopy in complex molecular materials

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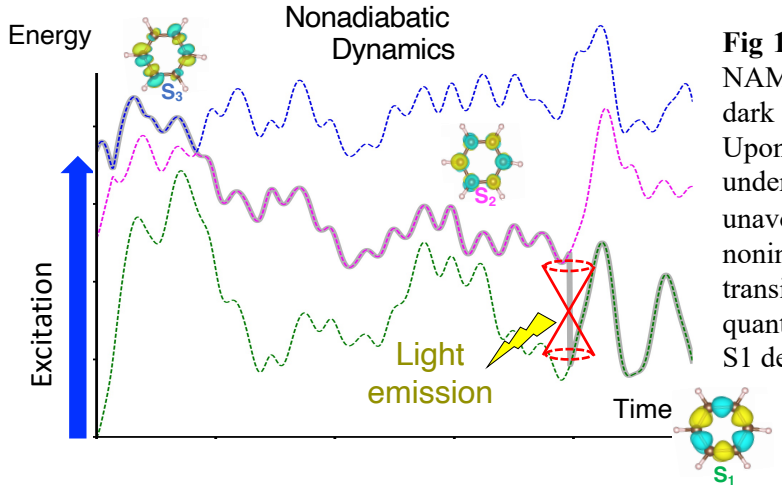

Fig 1. Schematic of a typical trajectory from a SH-NAMD simulation for a benzene molecule. The dark solid line represents the active trajectory path. Upon initiation on the S3 state, benzene rapidly undergoes internal conversion to S2 through trivial unavoided crossing between weakly or noninteracting adiabatic states. Then the S2 → S1 transition is enabled by surface hopping. The quantum transition between electronic states S2 and S1 depends on their nonadiabatic coupling strength

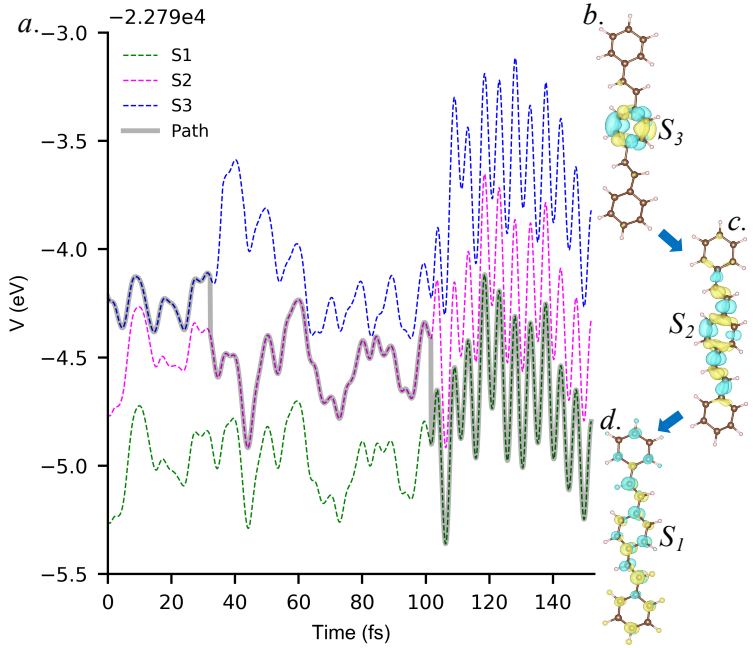

Fig 2. A demonstration of SH-NAMD simulation in photoinduced dynamics of a trans-distyrylbenzene. (a) shows the internal conversion S3 → S2 → S1 over a span of 140 fs. A strong vibrational excitation in all three potential energy profiles is observed right after the second hop, showing electronic energy transfer into nuclei motions. (b)−(d) shows the orbital representation of the transition density (TD) for states S1−S3. The energy transfer can be seen by following the dynamics of TD. The TD initially localized on the central ring at S3, expands to the two side rings through the C=C bond bridge at S2, and finally getting fully delocalized to all three rings at S1.

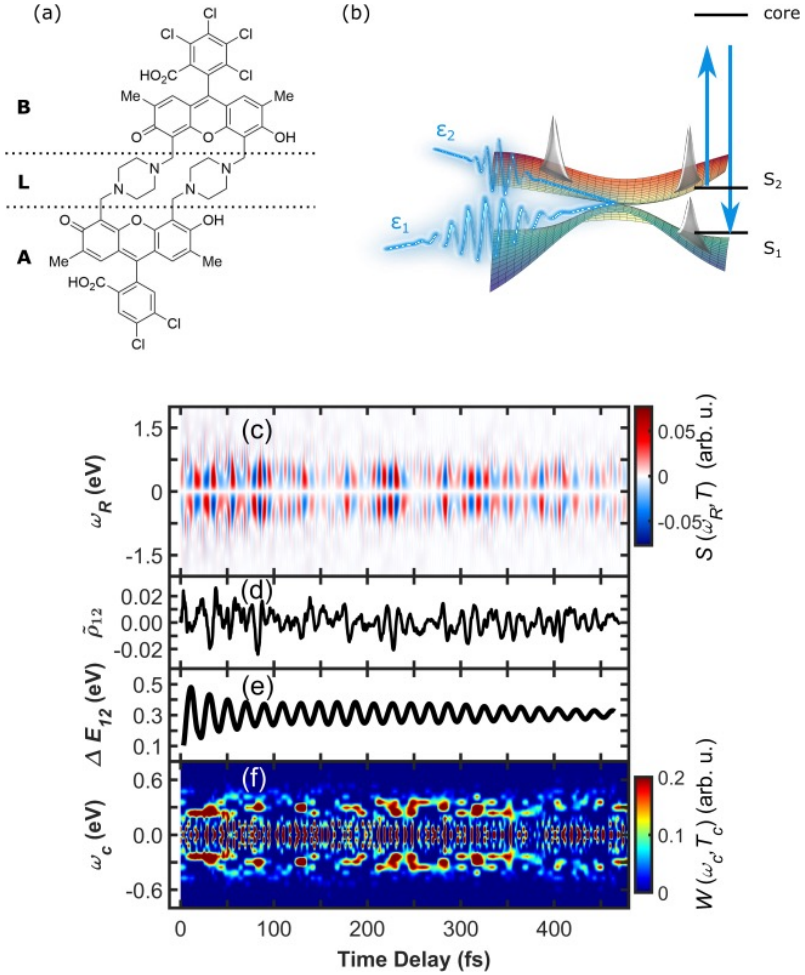

Fig 3: Stimulated X-Ray Raman spectroscopy on a heterodimer to monitor coherences. **a)** Molecular structure, with the two monomers A and B and the linker L. **b)** TRUECARS measurement, employing the X-Ray fields ε_0 and ε_1, inducing an off-resonant stimulated Raman process to detect coherences between the electronic states. **c)** TRUECARS signal according to equation (1). **d)** Average coherence magnitude over all 472 trajectories. **e)** Average energy splitting between S_2 and S_1. **f)** Wigner spectrogram of the TRUECARS signal. The main feature at $\omega_c = 0.3$ eV correctly maps the energy splitting.